III.A.14 Reliability and Durability of Materials and Components for Solid Oxide Fuel Cells

Objectives

- To support the SECA industrial teams towards the development of reliable and durable SOFCs.
- To support SECA Core Technology Program (CTP) modeling efforts by establishing material property databases.
- To establish failure criteria for SOFC materials and components associated with thermal fatigue and other degradation mechanisms.
- To determine the fracture behavior of SOFC materials and their interfaces.

Approach

- Standardized test methods were employed to determine the thermal and mechanical properties of SOFC materials.
- Scanning electron microscopy and spectroscopic techniques were used to characterize the evolution of the microstructure and the composition of SOFC materials when subjected to thermal cycling and thermal aging.
- The fracture behavior of SOFC materials and their interfaces was investigated by the load relaxation in double-torsion and by the four-point bending of bi-material notched test specimens with symmetrical interfacial cracks.
- Focused ion beam micromachining techniques were used to prepare test specimens to determine the fracture toughness of interfaces in SOFC material.

Accomplishments

- Developed methodologies and experimental facilities to assess the resistance of SOFC materials to thermal cycling and thermal aging.
- Determined the thermal properties of Ni-YSZ as a function of temperature and porosity.
- Characterized the microstructure of Ni-YSZ materials after thermal cycling and thermal aging.
- Developed microfabrication techniques to prepare bimaterial notched four-point bending test specimens with symmetrical interfacial cracks for the determination of interfacial toughness.

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Introduction

The durability and reliability of SOFCs are not only defined in terms of their electrochemical performance, but also by the ability of their components to withstand mechanical stresses that arise during processing and service. Specifically, the mechanical reliability and durability of the SOFC is determined by the stress distribution to which its components are subjected and by their distribution of strengths. The stress distribution is a complex function of several parameters that include the geometry of the SOFC, the properties of its components, the temperature distribution and external mechanical loads. The determination of the stress distribution in SOFC materials and components requires the use of computational tools (e.g., computational fluid dynamics and finite-element stress analyses), which in turn require knowledge of their physical and mechanical properties. The stochastic distribution of strengths of SOFC materials is primarily determined by the type and distribution of strength-limiting flaws, which are intrinsic to the material or that are introduced during processing and/or manufacturing.

During normal operation SOFC materials and components will experience large-amplitude low-frequency thermal cycles as a result of start-ups and shutdowns, and small-amplitude high-frequency thermal cycles during transients that are intrinsic to the operation and control processes of the SOFC. Under such operational conditions, the long-term reliability (durability) of SOFCs will be dictated in great measure by the resistance of the SOFC materials and components to degradation mechanisms that become activated during thermal cycling and thermal aging. These degradation mechanisms, which include creep deformation, thermal fatigue and slow-crack growth will not only affect the distribution of strengths of the material with time, but they will also affect the distribution of stresses to which these are subjected, including residual stresses.

Therefore, the development of reliable and durable SOFCs requires that the mechanisms responsible for the degradation of their materials and components be identified and characterized.

Approach

The Ni-based materials used in this investigation were prepared from a powder mixture of 75 mol% NiO and ZrO_2 stabilized with 8 mol% Y_2O_3 (YSZ). Different amounts of organic pore former (0, 15 or 30 vol% rice starch) were added to the powder mixture to obtain test specimens with different levels of porosity. Green test specimens were prepared by tape casting four 250-µm thick layers, which were subsequently laminated. A 15-µm thick layer of YSZ was screen-printed over some of the NiO-YSZ test specimens to obtain bi-layers. Mono- and bi-layer discs were sintered at 1,400°C in air for 2 hours and subsequently reduced in a 4%H_2+96%Ar gas mixture at 1,000°C. The weight of the test specimens was determined before and after reduction to confirm that NiO had been completely reduced to metallic Ni. The porosity of all test specimens was determined by alcohol immersion. A technique was developed to metallographically prepare thin bi-layer test specimens without having to embed them in a medium (e.g., epoxy). This became necessary to allow for the periodic microstructural examination of test specimens after they had been subjected to a predetermined number of thermal cycles or thermal aging time. The microstructure of bi-layer test specimens was characterized using scanning electro microscopy while energy dispersive x-ray spectroscopy (EDXS) was used to perform chemical analyses and to obtain elemental map distributions. Quantitative image analysis was used to assess microstructural changes in SOFC materials.

The fracture toughness, K_{IC}, and slow-crack growth behavior of SOFC materials were determined using the double torsion test method. Double torsion test specimens consisted of rectangular plates (20 mm in width, 40 mm in length) with notches 1 mm in width and 12.5 mm in length that were cut into one side of the test specimen using a circular diamond blade. The notch tip was machined such that the thickness of the test specimen at the notch tip tapered from very thin to the full thickness. The fracture tests were performed using a fixture fabricated out of alumina. Prior to testing, all notched test specimens were pre-cracked by loading the test specimen at a rate of 0.01 mm/min in a double torsion fixture. The reduction in the thickness at the notch tip facilitated the formation of a sharp pre-crack at relatively low loads, well below that required to cause fast fracture of the test specimen.

The slow crack growth behavior of SOFC materials was determined using the load relaxation version of the double torsion test configuration. According to this test procedure, a pre-cracked double-torsion test specimen is fast loaded at a constant displacement rate of 2 mm/min up to a load equivalent to 95% of the load associated with the fracture toughness of the material at particular temperature. At that point, the crosshead displacement of the mechanical testing machine is arrested and the load is monitored and recorded as a function of time. Under those conditions, cracks propagate in a stable manner, resulting in the relaxation of the load.

Focused ion beam and laser micromachining techniques were used to prepare notches in test specimens for the determination of the fracture toughness of Ni-YSZ/YSZ and YSZ/LSM interfaces according to a test method in which bi-material notched test specimens with symmetrical interfacial cracks are subjected to four-point bending.

Results

During FY 2005 work was carried out to quantify the effect of thermal cycling on the properties of Ni-YSZ and YSZ/Ni-YSZ bi-layers. These test specimens were subjected to thermal cycles between 100°C and 800°C under a constant flow rate (100 cc/min) of a gas mixture of 4%H_2 and 96%Ar. To distinguish between the effects of thermal exposure at 800°C from those that could result from thermal cycling on the physical and mechanical properties of these materials, thermal aging tests were carried-out at 800°C. Changes in the curvature of test specimens suggested that the residual stresses in bi-layer test specimens relax rapidly after a few cycles, or short periods of aging time, and that subsequently these stresses remain more or less constant. It had also been found that while the porosity and elastic modulus of YSZ/Ni-YSZ bi-layers do not change significantly with the number of thermal cycles or thermal aging time, their characteristic strength decreased by as much as 20%.

During FY 2006, these studies were continued and efforts were focused to identify relationships among the observed changes in the state of residual stress and mechanical properties of YSZ/Ni-YSZ bi-layers and any microstructural changes that might have occurred in these materials as a result of thermal cycling or thermal aging. The microstructure of these materials was characterized by scanning electron microscopy. To determine if any changes had occurred in the microstructure of these materials, a fixed region of the test specimen was analyzed periodically after a predetermined number of thermal cycles or thermal aging time. To facilitate monitoring potential changes at different scales, a collage of high-magnification images was obtained in each case. Figure 1 shows a scanning electron micrograph of a Ni-YSZ/YSZ bi-layer test specimen in which a 30% volume fraction of pore former had been used. The region of the test specimen that was used to monitor the occurrence of potential microstructural changes has been identified. Also shown

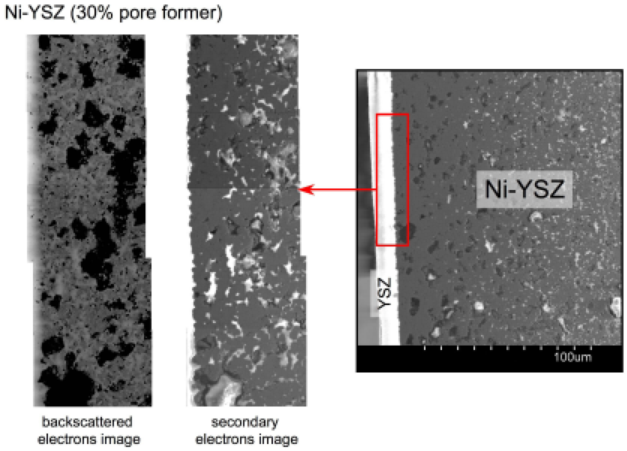

FIGURE 1. Scanning electron micrograph of Ni-YSZ/YSZ bi-layer test specimen (30% pore former). The red frame identifies the region that was characterized to track microstructural changes. Also shown is the backscattered electron image.

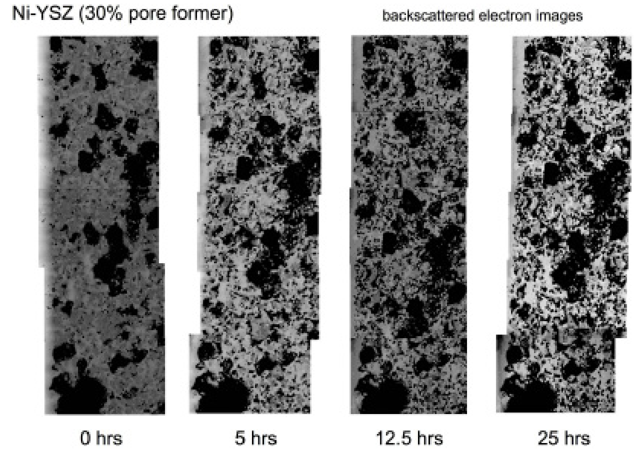

FIGURE 2. Backscattered Electron Images of Ni-YSZ/YSZ Bi-Layer Test Specimen (30% pore former) after Various Periods of Aging Time at 800°C

in Figure 1 is the backscattered electron image (BSE) of this region.

Figure 2 shows a collection of BSE images obtained for this test specimen after 0, 5, 12.5 and 25 hours at 800°C. Although the brightness in BSE images is directly proportional to the atomic number of the material being analyzed, the use of EDXS elemental maps became necessary to complement information provided by the BSE images, which in some cases can't be used to distinguish among the various phases in these materials. In each case elemental maps for nickel, oxygen and zirconium were obtained using EDXS. The images associated with the distribution of these elements for a Ni-YSZ/YSZ bi-layer test specimen in which a 30% volume fraction of pore former had been used, after 25 hours at 800°C are shown in Figure 3. To provide a uniform criterion to assess microstructural changes, a quantitative analysis of these images was performed using a commercial computer program as illustrated in Figure 4. In this analysis, each particle, grain or pore is identified and its dimensions are recorded and monitored as a function of aging time. Similar analyses have been performed for test specimens that have been subjected to thermal cycling. At the time of the preparation of this report, this work was in progress.

Slow crack growth is a phenomenon in which cracks grow in a material assisted by stress and the environment. It is known that hydrogen and water vapor, which are environments that are present in SOFCs, can induce slow-crack growth in materials that are being used to manufacture SOFCs. Therefore, the determination of the propensity of SOFC materials to embrittlement by hydrogen or water vapor is necessary to develop durable SOFCs.

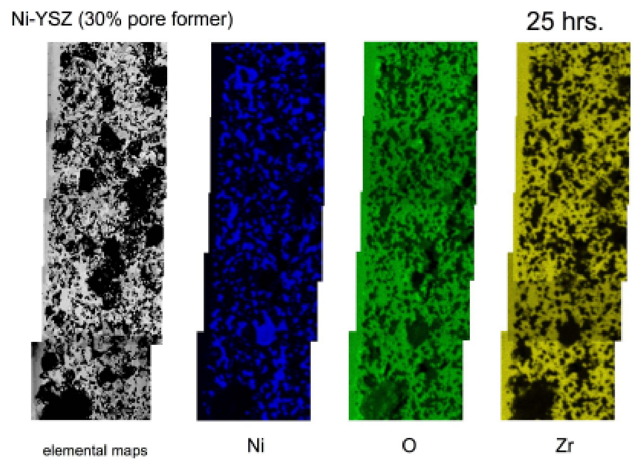

FIGURE 3. Elemental Maps for Nickel, Oxygen and Zirconium for a Ni-YSZ/YSZ Bi-Layer Test Specimen (30% pore former) after 25 Hours Aging at 800°C

The fracture toughness and slow-crack growth resistance of Ni-YSZ in a gas mixture of 4% H_2 and 96% Ar were found to decrease significantly with temperature. Figure 5 presents data for the fracture toughness of Ni-YSZ test specimens (30% volume concentration of pore former). Analysis of the fracture surfaces of these test specimens revealed the existence of Ni ligaments bridging the wake of the main crack (Figure 6). The plastic deformation of Ni grains at the crack tip is probably responsible for the tougher behavior of Ni-YSZ compared to NiO-YSZ. However, the concentration of plastically deformed Ni ligaments decreased with test temperature. To assess the sensitivity of these materials to hydrogen embrittlement, the fracture toughness Ni-YSZ test specimens was evaluated

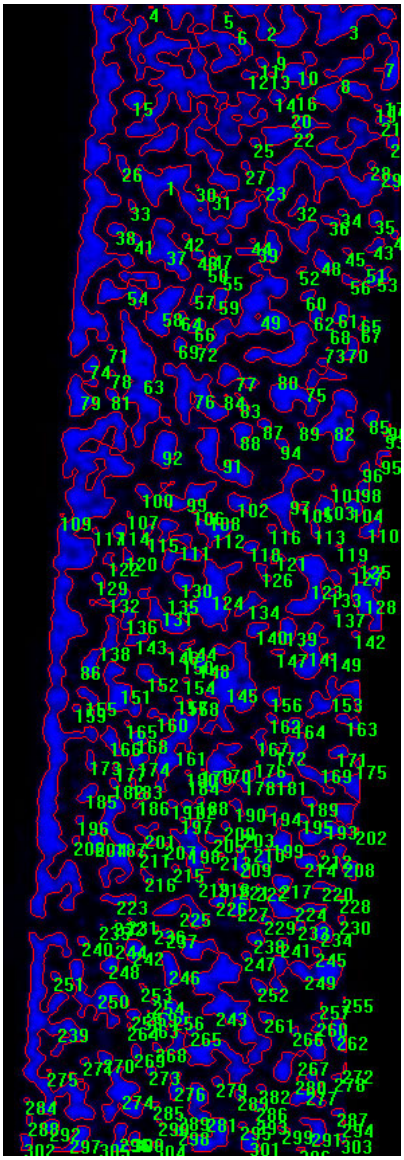

FIGURE 4. Quantitative Analysis of Elemental Map for a Ni-YSZ/YSZ Bi-Layer Test Specimen (30% pore former) after 25 Hours Aging at 800°C

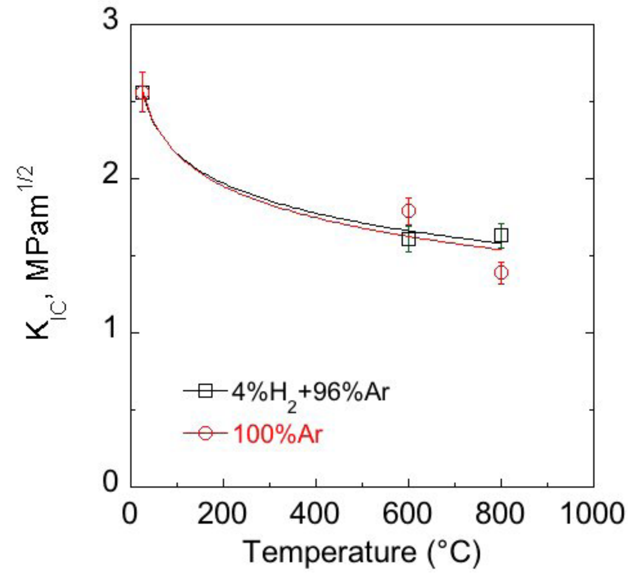

FIGURE 5. Fracture toughness of Ni-YSZ as a function of temperature. Data are presented from tests performed in a gas mixture of 4%H_2+96% Ar or in 100% Ar.

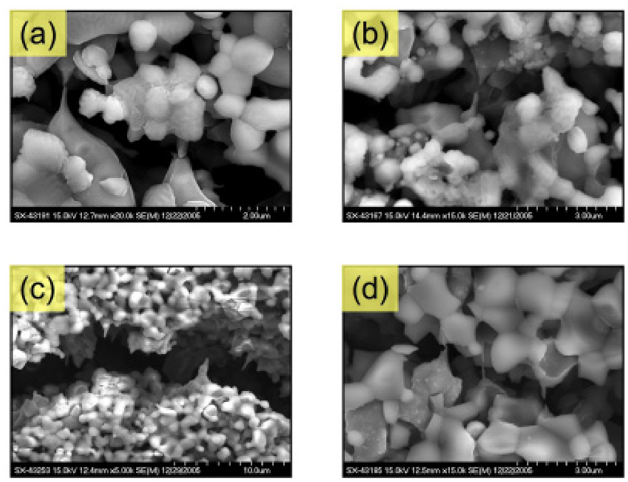

FIGURE 6. Scanning Electron Micrographs Illustrating Ni Ligaments in the Wake of a Crack after Fracture Toughness Tests for (a) and (b) Ni-YSZ (0% pore former) at Room Temperature, (c) Ni-YSZ (30% pore former) at 600°C and (d) Ni-YSZ (30% pore former) at Room Temperature

at 600 and 800°C in pure argon and it was found that a reducing environment with up to 4% hydrogen does not affect the fracture behavior of Ni-YSZ at these temperatures (Figure 5). It was also found that the threshold stress intensity factor for the onset of slow-crack growth decreases with temperature and with the porosity of the material and while the slow-crack growth exponent decreases with increasing temperature it decreases with porosity.

Delamination between the different layers in a SOFC has been identified as a potential damage mechanism that could affect the electrochemical performance of cells. During FY 2006, work was initiated to identify and implement test methods to determine the fracture toughness of these interfaces. Subsequently, the occurrence of changes in interfacial fracture toughness as a result of thermal cycling and thermal aging will be investigated. A bi-material notched four-point bending specimen with symmetrical interfacial cracks was selected to determine the fracture toughness of SOFC interfaces. Although this test method has been used successfully to evaluate the interfacial properties of several engineering systems, its applicability of test specimens that are a few

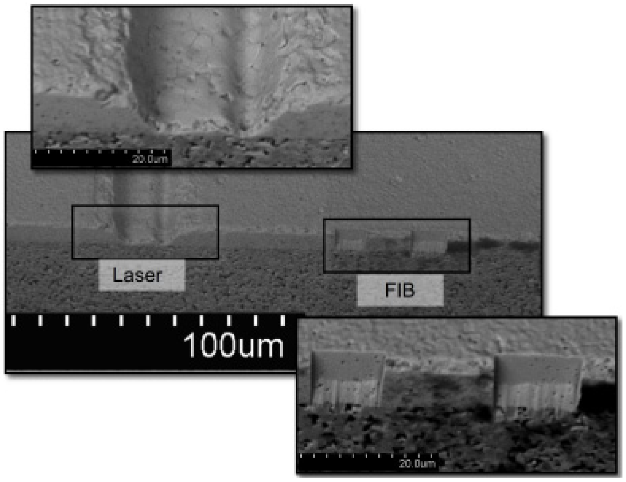

FIGURE 7. Scanning Electron Micrographs Illustrating Notches Made with Laser and Focused Ion Beam to Prepare Test Specimens for the Determination of Interfacial Fracture Toughness

micrometers in thickness, such as those being analyzed here, poses significant challenges. Both focused ion beam and laser micromachining techniques have been used to prepare these specimens as shown in Figure 7 in order to meet the requirements of a sharp notch that would initiate an interfacial crack. At the time this report was prepared, this work was in progress.

Summary

The development of models to predict the reliability and durability of SOFCs requires knowledge of the physical, electrochemical and mechanical properties of the SOFC materials and components and how these properties change with time under the influence of factors such as stress, temperature and environment. During FY 2006, work continued towards the goal of supporting the development of models to predict the reliability and durability of SOFCs. For example, it was found that while the fracture toughness of Ni-YSZ decreases both with temperature and with the porosity of the material, it was not affected by the presence of H_2 (up to 4% concentration) in the environment. During normal operation SOFC materials and components will experience large-amplitude low-frequency thermal cycles as a result of start-ups and shutdowns, and small-amplitude high-frequency thermal cycles during transients that are intrinsic to the operation and control processes of the SOFC. The effect of thermal cycling and thermal aging on the physical and mechanical properties of SOFC materials was investigated and work is in progress to establish relations between potential changes in the microstructure of these materials and the changes that have been observed in their properties. Work will continue to support the activities of the SECA Core Technology Program and the SECA industrial teams towards the design and demonstration of reliable and durable SOFCs.

FY 2006 Publications/Presentations

1. E. Lara-Curzio, M. Radovic, R. M. Trejo, K. L. More, T. R. Watkins, "Effect of Thermal Cycling and Thermal Aging on the Mechanical Properties of, and Residual Stresses in, Ni-Ysz/Ysz Bi-Layers," *Ceramic Engineering and Science Proceedings*, **27**, Issue 2 (2006).

2. J. Salem, M. Radovic and E. Lara-Curzio, "Using the Double-Torsion Test Method to Determine the Fracture Toughness of Thin Ceramic Plates," *Ceramic Engineering and Science Proceedings*, **27**, Issue 2 (2006).

3. M. Radovic and E. Lara-Curzio, "Fracture Toughness and Slow-Crack Growth Behavior of Ni-YSZ and YSZ as a Function of Porosity and Temperature," *Ceramic Engineering and Science Proceedings*, **27**, Issue 2 (2006).

4. M. Radovic, E. Lara-Curzio, R. Trejo, H. Wang and W. D. Porter, "Thermo-Physical Properties of Ni-YSZ as a Function of Temperature and Porosity," *Ceramic Engineering and Science Proceedings*, **27**, Issue 2 (2006).

5. E. Lara-Curzio, M. Radovic, R. M. Trejo, K. L. More, T. R. Watkins, "Effect of Thermal Cycling and Thermal Aging on the Mechanical Properties of, and Residual Stresses in, Ni-Ysz/Ysz Bi-Layers," Presented at the *30th International Conference & Exposition on Advanced Ceramics and Composites*, Cocoa Beach, FL, January 22-27 (2006).

6. J. Salem, M. Radovic and E. Lara-Curzio, "Using the Double-Torsion Test Method to Determine the Fracture Toughness of Thin Ceramic Plates," Presented at the *30th International Conference & Exposition on Advanced Ceramics and Composites*, Cocoa Beach, FL, January 22-27 (2006).

7. M. Radovic and E. Lara-Curzio, "Fracture Toughness and Slow-Crack Growth Behavior of Ni-YSZ and YSZ as a Function of Porosity and Temperature," Presented at the *30th International Conference & Exposition on Advanced Ceramics and Composites*, Cocoa Beach, FL, January 22-27 (2006).

8. M. Radovic, E. Lara-Curzio, R. Trejo, H. Wang and W. D. Porter, "Thermo-Physical Properties of Ni-YSZ as a Function of Temperature and Porosity," Presented at the *30th International Conference & Exposition on Advanced Ceramics and Composites*, Cocoa Beach, FL, January 22-27 (2006).